The Use of Silicone Wristbands as Passive Samplers for Measurement of Wood Smoke Analytes

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Alice Giem, Chris Palmer, and many data providers

UNIVERSITY OF MONTANA COLLEGE OF HUMANITIES & SCIENCES CHEMISTRY AND BIOCHEMISTRY

Significance and Impact

Each year in Montana there is a "fire season" during the late summer and fall months. Every Montanan knows the effects of smoke exposure, like difficult breathing, irritation of the eyes, and headaches.[1] Wood smoke from wildfires produced can travel as far as 4,000 miles from its source.[2] The smoke exposure can also lead to higher rates of influenza infection during flu season.[3]

Wood smoke contains many kinds of chemical compounds that are considered harmful for the general population. For wildlands firefighters (WLFFs), their exposure levels are much higher than for the general population.

Past research focused on particulate matter produced or used liquid condensates of smoke to quantify the compounds produced, but this failed to quantify the compounds that would be inhaled.

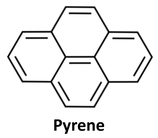
Unobtrusive and quantitative methods are needed to determine exposures of WLFFs and the general public to toxic compounds in wood smoke. The use of silicone wristbands as passive samplers has been proposed. However, previous analytical methods for wristbands have used large quantities of hazardous solvent and have shown poor recoveries for volatile wood smoke components.

The goal of this research was to develop, evaluate, and demonstrate analytical methods that generate less hazardous chemical waste while also providing improved analytical recoveries of selected wood smoke markers from silicone wrist bands.

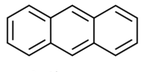
To achieve this goal, we have adjusted previous methods to lessen the quantities of chemical solvents used by more than 60%. It was hypothesized that evaporative losses of volatile compounds would also be reduced by this approach because smaller solvent volumes allow shorter evaporation periods.

Wood Smoke Chemical Markers Considered

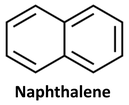
Polycyclic Aromatic Hydrocarbons (PAHs)



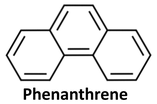
Pyrene



Anthracene

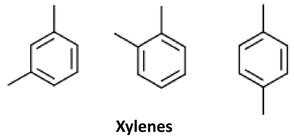


Naphthalene

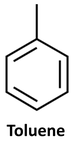


Phenanthrene

Volatile Organic Compounds (VOCs)



Xylenes



Toluene

Benzene

Methodology and Data

Wristbands were first cleaned with two consecutive solvent baths of ethyl acetate, hexane, and methanol. After drying, wristbands were exposed to known quantities of chemical markers. After exposure and equilibration, analytes were extracted using 30-40 mL of ethyl acetate (reduced from 100 mL in previous methods). Extractions were reduced to 2 mL under filtered air and then tested by gas chromatography-mass spectrometry (GC-MS). Extracted ion chromatograms (EIC) were generated at masses 91, 128, 178, and 202 for toluene and xylenes, naphthalene, phenanthrene and anthracene, and pyrene, respectively. Integrated peak areas in EIC of marker standard solutions (0.1ng/mL, 17.5ng/mL, and 35ng/mL) were used to determine response factors:

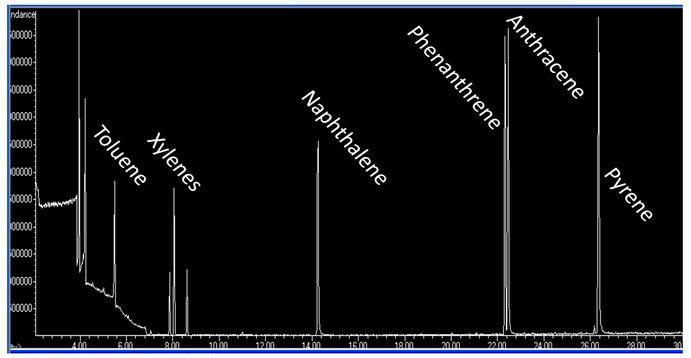
$$\frac{\boldsymbol{Area}}{[\boldsymbol{Concentration}]} = \boldsymbol{Response\ Factor}$$

The integrated peak areas in EICs of wristband extracts were used to find extract concentrations:

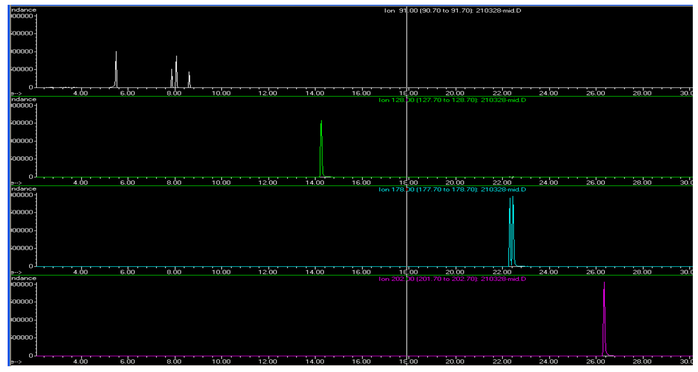
$$\frac{\boldsymbol{Area}}{\boldsymbol{Response\ Factor}} = [\boldsymbol{Concentration}]$$

Recoveries were then calculated from the measured and theoretical concentrations:

$$\%\boldsymbol{Recovery} = \boldsymbol{100} * \frac{[\boldsymbol{Concentration}]}{[\boldsymbol{Theoretical\ Concentration}]}$$



A mass spectrum from a standard solution made for spiking wristbands, showing peaks for toluene, xylenes, naphthalene, phenanthrene, anthracene, and pyrene.



Extracted Ion Chromatograph from the mass spectrum graph above. These peaks correspond to different ion masses: 91, 128, 178, and 202 respectively.

Results

The table below contains the percent yield for each analyte using the analysis methods above for each of the 3 spike levels.

	Toluene	Xylenes (1)	Xylenes (2)	Xylenes(3)	Naphthalene	Phenanthrene	Anthracene	Pyrene
0.1 ng/mL	16.6	32.5	34.8	39.1	50.4	47.5	30.8	41.7
17.5 ng/mL	26.5	45.7	62.3	55.8	97.2	102.3	96.8	111.6
35.0 ng/mL	30.8	51.0	68.6	60.7	96.9	98.8	103.0	105.3

- Good analytical recoveries (≥ 80%) for low volatility markers at high and intermediate concentration levels indicate that extractions with lower solvent volumes are effective.
- Poor analytical recoveries (≤ 50%) for volatile analytes demonstrate that evaporative losses are still significant.
- Poor analytical recoveries for wristbands spiked at low levels indicate either losses of markers to adsorption on surfaces or through evaporation.

Discussion and Conclusions

This research demonstrated that the chemical waste produced by this analytical method, particularly for semi-volatile compounds at relatively high concentrations, can be effectively reduced by using approximately 1/3 of the volume of extraction solvent. However, the reduced solvent volumes, while they do reduce evaporation times, do not lead to improved recoveries of volatile markers. Poor analytical recoveries for wristbands spiked at low levels indicate either losses of markers to surfaces or through evaporation. This could be addressed through use of an appropriate internal standard.

Challenges and Continued Research

Challenges of Methodology:

- Blank vials consistently had noise that was not observed in samples (but insignificant levels of target marker compounds).
- Volatile compounds such as Benzene can not be extracted with sufficient recovery due to evaporative losses.

This research is ongoing, and these are the next steps:

- Exposure of wristbands in a smoke exposure chamber.
- Adjustment and improvement of cleaning method.
- Development and implementation of zero-solvent head-space analysis for volatile components.

References

(1) How to Treat Smoke Inhalation: Symptoms, Signs, Causes & Recovery https://www.emedicinehealth.com/smoke_inhalation/article_em.htm (accessed Apr 9, 2021).
(2) How Far Can Wildfire Smoke Travel? | Fire Restoration Blog https://emasterfinder.com/cleaning-blog/how-far-can-wildfire-smoke-travel/ (accessed Apr 9, 2021).
(3) Landguth, E. L.; Holden, Z. A.; Graham, J.; Stark, B.; Mokhtari, E. B.; Kaleczyc, E.; Anderson, S.; Urbanski, S.; Jolly, M.; Semmens, E. O.; Warren, D. A.; Swanson, A.; Stone, E.; Noonan, C. The Delayed Effect of Wildfire Season Particulate Matter on Subsequent Influenza Season in a Mountain West Region of the USA. *Environ. Int.* **2020**, *139*, 105668. https://doi.org/10.1016/j.envint.2020.105668.

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